Normal-state anomalies in the transport and magnetic properties in the $(La_{1-x}Pr_x)_{1.85}Sr_{0.15}CuO_4$ system and their correlation with T_c suppression: A signature of the effects of orthorhombic distortions

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(Received 25 March 1998)

The correlation between the normal-state anomalies observed in the magnetic and transport properties of the $(La_{1-x}Pr_x)_{1.85}Sr_{0.15}CuO_4$ system with $0 \leqslant x \leqslant 0.5$ was studied. The x-ray-diffraction patterns revealed a linear increase of the $(a-b)$ orthorhombic parameter with the Pr content. The resistivity curves showed an increasing deviation from linearity below ~100 K. This anomaly was properly accounted by a logarithmic term, whose coefficient C linearly increases with x. Superconducting quantum interference device measurements of the normal-state magnetic susceptibility evidenced a deviation from the Pr^{3+} Curie-Weiss behavior in the same temperature range for which the resistivity anomaly occurs. This behavior is explained in terms of an induced magnetic moment at the CuO_2 layers under strain. A Dzialoshinsky-Moriya interaction, associated to the orthorhombic distortions, is proposed to be the source of a weak canted ferromagnetic component, which develops in conjunction with an enhancement of the antiferromagnetic correlations. A comprehensive picture of the conduction mechanism for the whole system is presented in terms of a Kondo-like scattering of the mobile holes by the spin fluctuations at the conduction planes. T_c suppression was found to correlate with C, suggesting that the excitation which interacts with the carriers in the normal state is relevant for superconductivity. [S0163-1829(99)11505-4]

I. INTRODUCTION

It is believed that the unusual properties of the normal-state resistivity in the layered cuprates reflect the electronic structure that underlies high-T_c superconductivity. Some striking features are inconsistent with the electron-phonon scattering mechanism. At the hole concentration for optimum T_c, the in-plane resistivity $\rho_{ab}(T)$ is linear in a wide temperature range from just above T_c to nearly 1000 K.[1,2] The electron-phonon coupling is too small to account for this absence of resistivity saturation and the high value of T_c.[1] A T-linear resistivity has been observed down to 10 K in $Bi_2Sr_2CuO_6$, yielding a very low Debye temperature of 35 K in terms of electron-phonon scattering.[2] These facts require an alternative mechanism as the origin of the resistivity behavior.

The most plausible and frequently discussed option is scattering due to spin fluctuations in the CuO_2 planes. However, there has been no experimental result up to now providing definitive evidence for this mechanism. In part, this is due to the absence of a detailed comparison between the transport and magnetic properties for a suitable system.

In an effort to shed further light on this subject, we report here on the temperature dependence of the resistivity and the magnetic susceptibility of the $(La_{1-x}Pr_x)_{1.85}Sr_{0.15}CuO_4$ (Pr:LSCO) series. Pr was selected because its effects in the LSCO matrix are strictly steric in nature, as we discuss below. This way, the Cu spin dynamics is expected to be gradually modified by the induced distortions, allowing us to conduct a systematic study of the role of the magnetic interactions and the structural disorder. We have found a logarithmic divergence on cooling for the normal-state resistivity and that the anomalies observed in the magnetic susceptibility for $T > T_c$ can be consistently related to the charge transport features under the assumption that spin scattering is dominant. The changes in T_c promoted by doping clearly correlates with the parameters characterizing the conduction mechanism, suggesting that the excitation that interacts with the carriers in the normal state might play an important role in superconductivity.

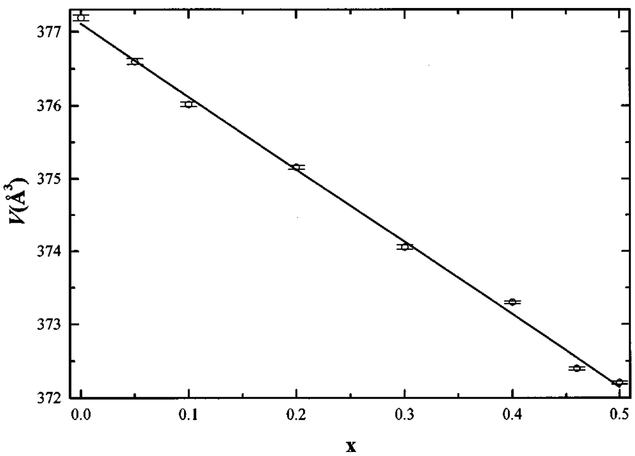

FIG. 1. The linear reduction of the cell volumes with the increase of the Pr content for samples of the $(La_{1-x}Pr_x)_{1.85}Sr_{0.15}CuO_4$ system. The straight line is a least-square fitting.

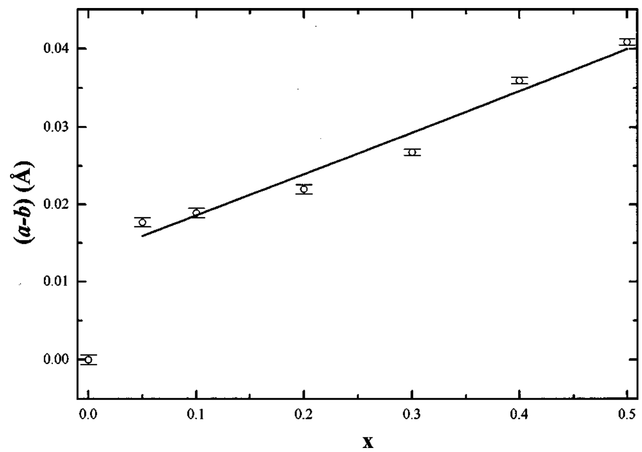

FIG. 2. The linear increase of the $(a\text{-}b)$ orthorhombic parameter with the Pr content for samples of the $(La_{1-x}Pr_x)_{1.85}Sr_{0.15}CuO_4$ system. The straight line is a fit for the Pr-doped samples.

II. EXPERIMENT

All the samples of the $(La_{1-x}Pr_x)_{1.85}Sr_{0.15}CuO_4$ system ($x=0.0,\ 0.05,\ 0.1,\ 0.2,\ 0.3,\ 0.4$, and 0.5) were obtained by a standard solid state reaction method. Stoichiometric amounts of high purity La_2O_3, Pr_6O_{11}, $SrCO_3$, and CuO were well mixed and pressed into pellets. The samples were sintered at 1150°C in an oxygen atmosphere for 24 h, with two intermediate treatments at 980° and 1000°C.

The room temperature x-ray diffraction patterns were collected in an automated Siemens type-F diffractometer in step-scanning mode ($10° \leqslant 2\Theta \leqslant 90°$). A high stability Philips PW1830/25 generator was used. Structure refinement was performed by a Rietveld analysis. Neutron diffraction data were collected at room temperature on approximately 0.5 g specimens using the position sensitive detector diffractometer at the University of Missouri Research Reactor, with a wavelength of 1.7875 Å.

The dc resistivity was measured in a computer data-logger system using a Keithley 224 high precision source and a Keithley 181 nanovoltmeter. High-quality silver painted contacts were obtained on the regular bars cut from the pellets. Normal-state magnetic susceptibility measurements were performed in a Quantum Design superconducting quantum interference device magnetometer at 0.5 T.

III. RESULTS

A. Structural details

The x-ray-diffraction patterns were the expected ones for the T structure of LSCO, no spurious lines being detected. Figure 1 shows the linear reduction of the cell volumes with doping, as determined from a Rietveld refinement of the data. Pr gradually promotes an orthorhombic distortion of the tetragonal LSCO matrix, evidenced by the linear increase of the orthorhombic parameter $(a\text{-}b)$, as shown in Fig. 2.

As the Pr-induced distortions proceed, the deviation from flatness of the CuO_2 planes increases, since the CuO_6 octahedra tilt about the (110) direction, promoting buckling. The average value of the Cu-O-Cu buckling angle φ [measured in the $(a\text{-}b)$ plane] was determined from neutron diffraction measurements; its dependence with x is shown in Fig. 3. The corresponding rate of decrease of T_c with φ is about 4 K for each degree of buckling. Tilting also involves a displacement of the apical oxygens O(A). The variation of the average O(A)-Cu bond length with the Pr content was determined, as shown in the inset of Fig. 3.

B. Resistivity measurements

Figure 4 shows the temperature dependence of the resistivity, $\rho(x,T)$, for the Pr:LSCO samples. As x increases, a systematic reduction of the midpoint T_c was observed, as shown in Fig. 5(a). The $\rho(x,T)$ curves are linear for $T \geqslant 100$ K, but exhibit an increasing upward deviation with the Pr content on cooling, without minima and upturns, as evidenced in the inset of Fig. 4 for $x=0.5$. The residual resistance $\rho(x,0\,\text{K})$, taken as the extrapolation of the linear behavior down to 0 K, smoothly increases up to 270 $\mu\Omega$ cm for $x=0.5$.

A variety of functional forms do not fit the diverging normal-state resistivity, including thermal activation ($\ln\rho \sim -1/T$), various types of variable range hopping conduction ($\ln\rho \sim T^{-\beta}$ with $\beta=\frac{1}{2},\frac{1}{3},\frac{1}{4}$), and power-law dependence

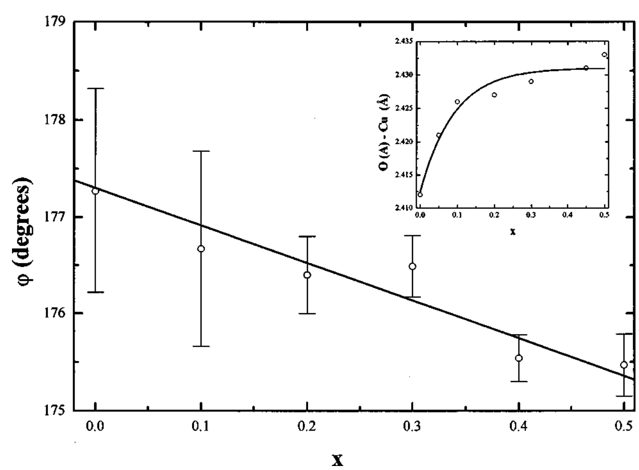

FIG. 3. The variation of the average *in-plane* Cu-O-Cu buckling angle φ with the Pr content. The straight line is a fit to the data. Inset: the expansion of the average O(A)-Cu bond length with x.

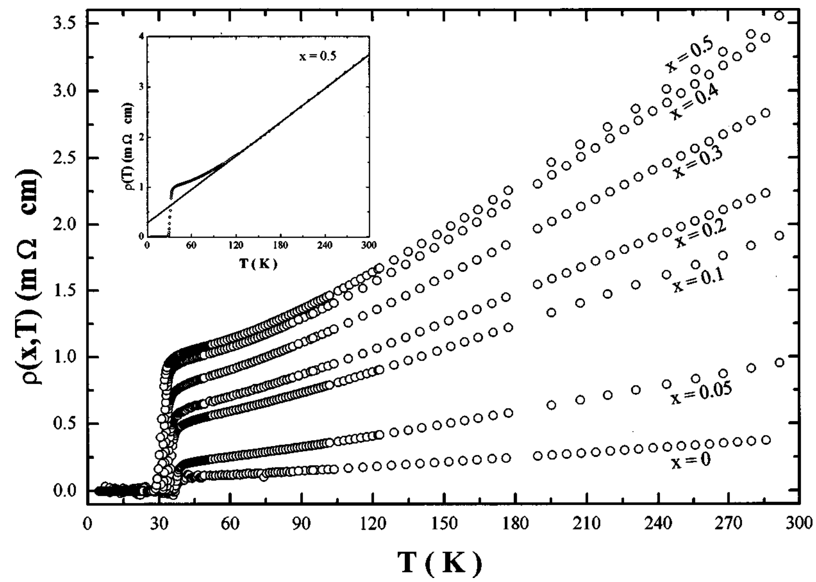

FIG. 4. Temperature dependence of the resistivity for samples of the $(La_{1-x}Pr_x)_{1.85}Sr_{0.15}CuO_4$ system. The upward deviation from linearity below ~100 K is shown in the inset for $x=0.5$.

($\ln\rho\sim\ln T$). Since a logarithmic divergence has been observed on cooling in different cuprates,[3–5] a

$$\rho(x,T)=A+BT-C\ln T \tag{1}$$

dependence was fitted to the experimental curves, with good results. The deviation from linearity $\Delta\rho(x,T)=\rho_{exp}(x,T)-A-BT$ is plotted against a $\ln T$ scale in Fig. 6 for $T_c\leqslant T\leqslant 100$ K. Except for a small region near to the superconducting transition, straight lines fit well all the curves, with coefficient C increasing linearly with x [see Fig. 5(b)]. As a consequence, T_c suppression correlates with the strength of the normal-state logarithmic divergence, as shown in Fig. 5(c).

The magnetoresistance (MR) of all the samples was measured up to 8 T at different temperatures. As x increases, a negative contribution, superimposed to the positive behavior of the LSCO matrix, becomes more evident. Figure 7 shows this effect for $x=0.4$ at $T=60$ K.

C. Magnetic measurements

Figure 8 shows the temperature dependence of the normal-state magnetic susceptibility, $\chi(x,T)$, for all the samples of the series. The solid lines are fits discussed later. At first sight, the measurements suggest a Curie-Weiss behavior, coming from the contribution of the Pr ions. However, a $1/\chi(T)$ vs T plot shows a downward deviation from the expected linear behavior below ~120 K for all the samples, as shown in the inset of Fig. 8 for $x=0.3$. Above this temperature, straight lines fit well with the data, giving an effective magnetic moment $\mu_{Pr}=3.52\mu_B$, which is close to the $3.58\mu_B$ reported for Pr^{3+},[6] and a Curie-Weiss temperature $\Theta_{Pr}=-9.5$ K (less than 3% in variation for all the samples). These results indicate that the effects of Pr in the magnetic response of the LSCO matrix cannot be described in the whole temperature range by simply adding a Pr^{3+} Curie-Weiss term, and that another contribution clearly reveals its presence when cooling below 120 K. Thus, fitting was attempted according to the expression

$$\chi(x,T)=\chi_0(T)+\chi_{Pr}(x,T)+\chi_{ind}(x,T), \tag{2}$$

where $\chi_0(T)$ is the measured curve for the Pr-undoped sample, $\chi_{Pr}(x,T)$ is the Pr^{3+} Curie-Weiss component (μ_{Pr} and Θ_{Pr} were kept constant during fitting) and $\chi_{ind}(x,T)=D_{ind}/(T-\Theta_{ind})$ is a second Curie-Weiss term which accounts for the Pr-induced effects. The continuous lines in Fig. 8 are the result of such fitting. The D_{ind} constants were found to linearly increase with x, as shown in Fig. 9, while Θ_{ind} is positive and moves close to 28 K for all the samples.

IV. DISCUSSION

The logarithmic contribution to the resistivity reminds us of several possible mechanisms: weak localization,[7] two-dimensional (2D) electron-electron interaction,[8] and the Kondo effect;[9] we discuss them below. Although the marginal Fermi-liquid model[10] for the normal-state properties of the high-T_c cuprates predicts a leading logarithmic correction to the resistivity for $T\rightarrow 0$, this behavior is observed in our samples far beyond the temperature range relevant for this channel.

Let us consider first the effect of disorder. The structural data and the increase of the residual resistivity with x evidence that the LSCO matrix is gradually distorted by doping. The expansion of the average O(A)-Cu bond length is also related to the disorder promoted at the CuO_2 planes, because a random potential scattering might be induced due to the local variation of the position of the apical oxygens in the neighborhood of the Pr ions. In conventional 2D disordered metals, a logarithmic correction to the resistivity can arise from coherent back-scattering or from electron-electron interaction, because they involve quantum-mechanical diffusion.[7,8] Both theories predict that the coefficient of the in-plane $\ln T$ conductance is $\sim e^2/h$ whenever the conductance is $\geqslant e^2/h$. Although our measurements were performed

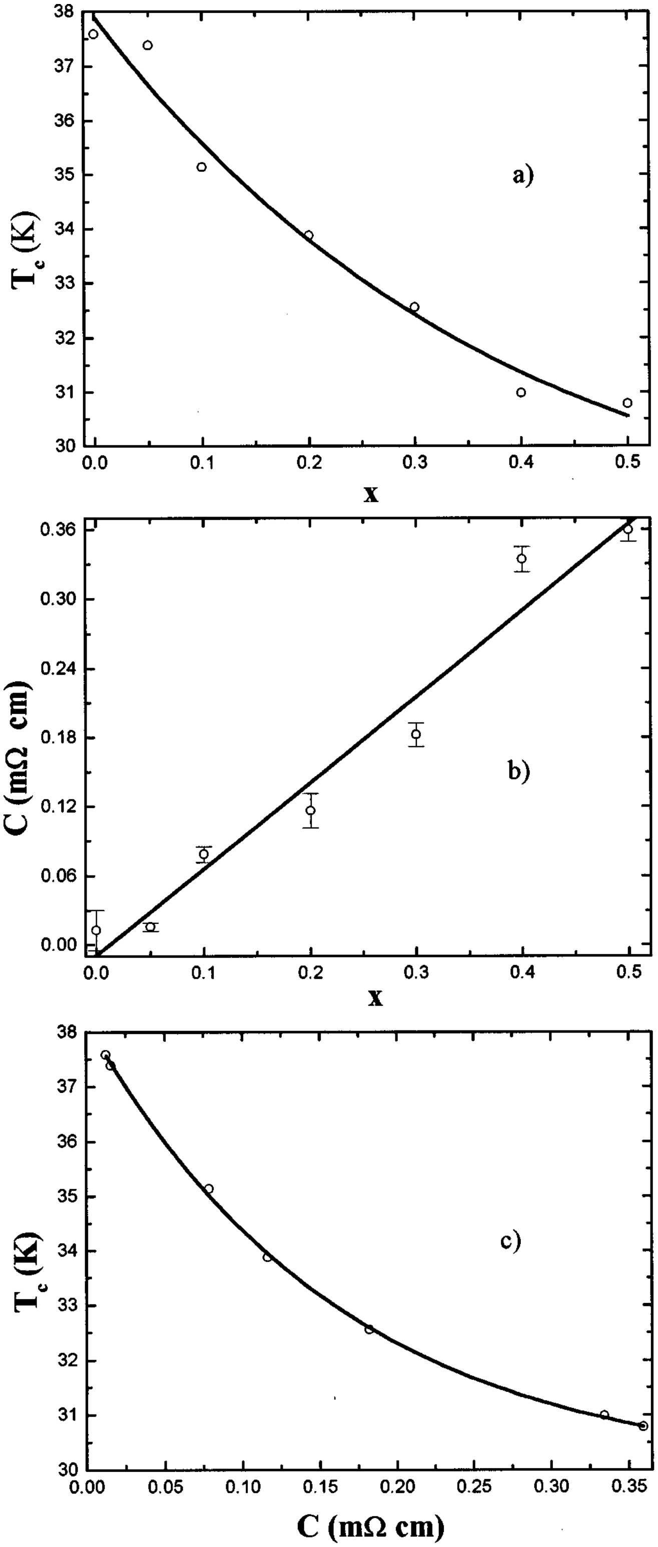

FIG. 5. T_c suppression (a) and the increase of the coefficient C of the logarithmic contribution to the resistivity (b) with the Pr content. The correlation of T_c with the coefficient C is shown in (c). The continuous lines are a guide to the eyes.

in polycrystalline samples, we verified that this condition is accomplished for all of them. These results appear at first sight to be consistent with localization and interaction effects as the source of the resistivity behavior. However, the MR measurements point in the other direction. Although negative MR has been never observed in $La_{1.85}Sr_{0.15}CuO_4$, it increasingly emerges in the Pr:LSCO series, competing with the positive background of the optimum Sr-doped LSCO. This effect is much larger than that usually found in 2D metals at such high temperature as 60 K.[7] At this temperature, the $\ln T$ component is a small fraction of all the conductance. This means that the magnetic field does not solely affect the $\ln T$ correction to the conductance as it does for coherent backscattering and interaction effects. In addition, the MR from the particle-hole scattering contribution to the electron-electron interaction is expected to be positive rather than negative.[8]

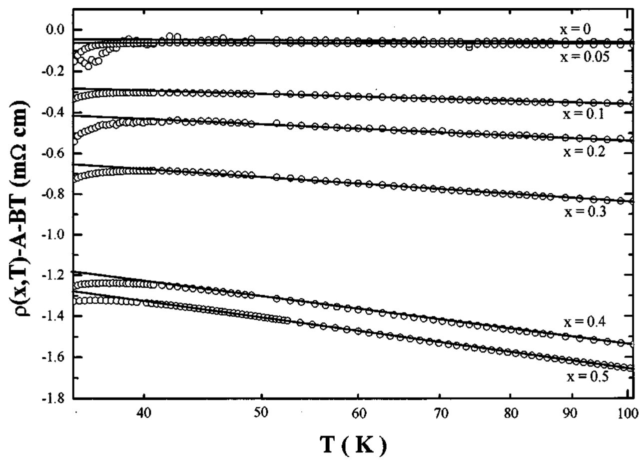

FIG. 6. The dependence of the nonlinear part of the resistivity $\Delta\rho=\rho_{\rm exp}-A-BT$ on $\ln T$ for samples of the $(La_{1-x}Pr_x)_{1.85}Sr_{0.15}CuO_4$ system. The straight lines represent the best fits to the data using Eq. (1).

Negative MR has been reported for the out-of-plane ρ_c resistivity, and even for the in-plane ρ_{ab} one, in several underdoped and nonsuperconducting layered cuprates, i.e., in systems with enhanced antiferromagnetic (AF) correlations. It has been also observed in a variety of metals containing fluctuating spins: Kondo systems and spin glasses.[11] The authors have ascribed this to a reduction of spin scattering by the magnetic field. Since for $H=4$ T and $T=60$ K the Zeeman-split levels are separated by a $g\mu_B SH$ energy less

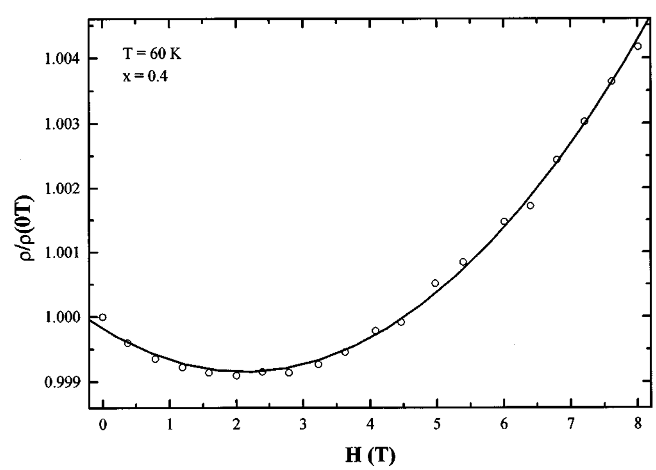

FIG. 7. The magnetoresistance for the $x=0.4$ sample of the $(La_{1-x}Pr_x)_{1.85}Sr_{0.15}CuO_4$ system at 60 K.

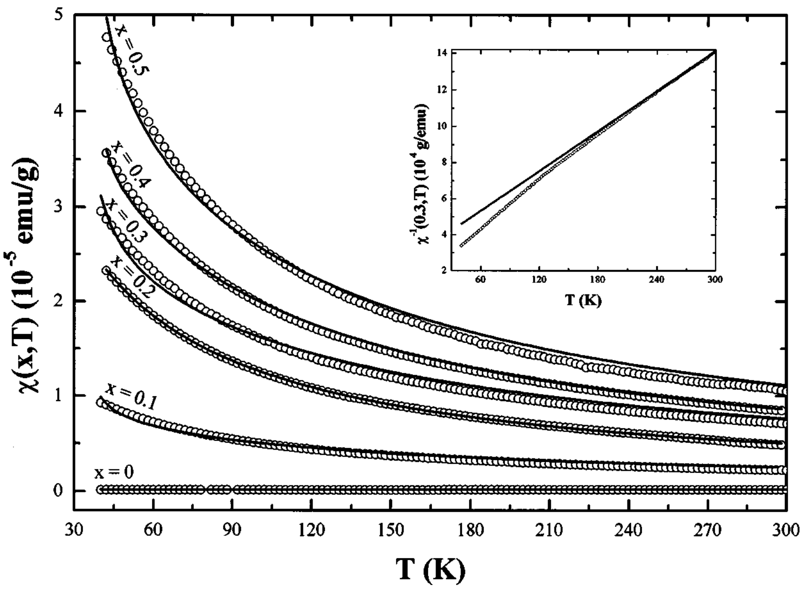

FIG. 8. Temperature dependence of the normal-state magnetic susceptibility for samples of the $(La_{1-x}Pr_x)_{1.85}Sr_{0.15}CuO_4$ system. The continuous lines are fittings as described in the text. Inset: temperature dependence of the inverse magnetic susceptibility for $x=0.3$; the straight line is a fitting in the 200–300 K interval extrapolated to 0 K.

than kT (taking $g=2$ and $S=\frac{1}{2}$), a similar mechanism would be at work in the Pr:LSCO series. These considerations suggest that the spin degrees would be relevant for the conduction mechanism.

On the other hand, disorder cannot account for the observed T_c suppression. It is generally true, regardless of models, that if nonmagnetic disorder is pair breaking, T_c will be affected only when the mean free path ℓ is reduced to below the coherence length ξ. From the residual resistivity $\rho(x,0\,\mathrm{K})$ we can calculate ℓ according to

$$\rho(x,\ 0\ \mathrm{K})=4\pi v_F/\omega_p^2\ell, \quad (3)$$

where v_F is the Fermi velocity and ω_p is the plasmon frequency. In $La_{1.85}Sr_{0.15}CuO_4$,[1] $\omega_p\approx 0.7\,\mathrm{eV}$, $v_F\approx 1\times 10^7\,\mathrm{cm\,s^{-1}}$ and ξ is about 15 Å. The lowest value of the mean free path is $\ell=36\,$Å for $x=0.5$, indicating that other mechanisms have to be considered to explain the reduction

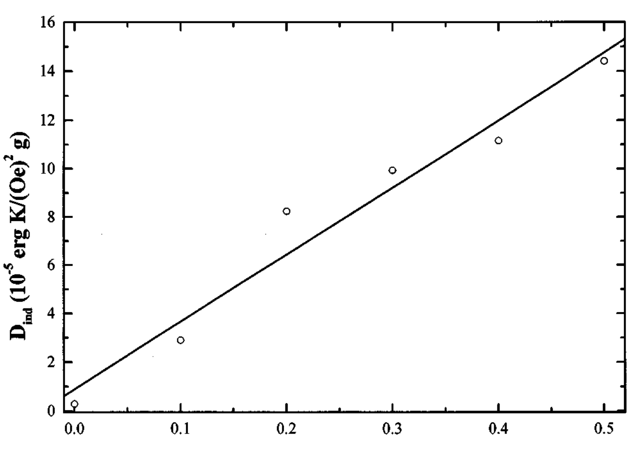

FIG. 9. The linear increase of the Curie-Weiss coefficient D_{ind} for the contribution to the magnetic susceptibility induced by the effects of distortions on the Cu spin system.

in T_c. The scattering lifetime derived from this data is $\tau=4\times 10^{-14}\,\mathrm{s}$; using the uncertainty principle, an energy spread ε over which the level widths are smeared by the scattering may be determined, giving $\varepsilon\cong 1050\,\mathrm{K}$, that is about the Cu spin-exchange energy J. This suggests that the scattering mechanism is dominated by coupling to low-energy excitations of the Cu spins, reinforcing the picture in which motion of the charge carriers would involve a rearrangement of the spin system in the CuO_2 layers. In summary, weak-localization effects and electron-electron interaction appear to be rather inconsistent to describe the MR measurements and T_c suppression.

We discuss now the spin-flip scattering channel as the possible origin for the $\ln T$ behavior. The fact that the resistivity starts to depart from linearity at approximately the same temperature for which the magnetic susceptibility curves deviate from the Pr^{3+} Curie-Weiss behavior strongly indicates that the magnetic interactions have a relevant role in the resistivity anomaly. For our samples, there are two possible sources for the Kondo-like behavior: a direct interaction of the carriers with the localized magnetic moment of the Pr ions or scattering by the Cu spin fluctuations. Pr was just chosen as the doping element because it is an out-of-plane substitution for which there is no evidence for tetra- or mixed valence or for hybridization with the electronic states of the conduction planes in LSCO,[12] leaving unchanged the hole concentration[13] and the oxygen content.[14] The effective magnetic moment of $3.52\mu_B$ obtained for the Pr ions from our $\chi(x,T)$ measurements confirms its 3+ state. So, there is no need for the search of other than steric reasons as the source of the observed transport and magnetic properties. Scattering by the spin fluctuations at the CuO_2 layers remains as the only possible source of the logarithmic deviation, with an intensity determined by the effects of the distortions on the spin dynamics. Thus, the physical meaning of $\chi_{\mathrm{ind}}(x,T)$ is the contribution to the magnetic susceptibility coming from the Cu spin system under strain; we interpret its behavior as follows.

As known, short-range dynamic antiferromagnetic (AF) correlations survive in the layered cuprates in the metallic compositions and even in the superconducting state,[15,16] with a correlation length that shortens with the increase in the concentration and mobility of the holes.[17,18] Since in the Pr:LSCO system the hole concentration remains constant even for large doping rates,[14] the systematic increase of the resistivity with x evidences a reduction in hole mobility, which would lead to an enhancement of the AF correlations. In principle, the emergence of broad maxima on cooling would be the expected signature of such enhancement in the $\chi(x,T)$ curves.[18] Instead, the changes consist of a linear increase of D_{ind} with the Pr content. From these values, a maximum induced moment of $0.01\mu_B$ per Cu ion was obtained. We explain this induced moment as a consequence of the orthorhombic distortions. In the La_2CuO_4-parent compound, the magnetic susceptibility exhibits a sharp increase when the long-range Néel temperature T_N is approaching on cooling, due to a ferromagnetic canted moment developed in conjunction with the AF correlations. This ferromagnetic component emerges as a consequence of a Dzialoshinsky-Moriya interaction, due to a local symmetry breakdown promoted by the orthorhombic distortions. The role of these distortions is essential: in $Sr_2CuO_2Cl_2$, which also has a T structure but remains tetragonal down to 10 K, the steep increase of $\chi(T)$ near T_c disappears.[18] We note that the value of the $(a\text{-}b)$ orthorhombic parameter for $x=0.5$ is similar to that of La_2CuO_4 at room temperature and that the Curie-Weiss temperature Θ_{ind} for the contribution from the Cu spin system is positive for the whole series. These results matches with the idea that the induced moment would have a canted ferromagnetic origin. This interpretation explains why an enhancement of the AF correlations with x manifests in the $\chi(x,T)$ measurements as an increasing Curie-Weiss upturn. Under this scheme, the linear increase of both C and D_{ind} with the Pr content represents that the spin scattering becomes more intense as the AF correlations are reinforced.

Finally, we found that T_c suppression clearly correlates with the intensity of the normal-state scattering mechanism, represented by the coefficient C, as shown in Fig. 5(c). This result strongly suggests that the interaction which determines the resistivity anomaly also acts as the leading pair breaking mechanism.

V. CONCLUSIONS

A systematic study of the transport, magnetic, and structural properties was conducted in the Pr:LSCO series. The normal-state anomaly observed in the resistivity was found to occur in the same temperature range for which magnetic susceptibility curves deviate from the Pr^{3+} Curie-Weiss behavior. Under the assumption that the logarithmic contribution to $\rho(T)$ comes from scattering of the carriers by the spin fluctuations in the CuO_2 planes, a consistent explanation for the whole series is given in terms of the effects of disorder on the Cu spin dynamics; other possible sources for the $\ln T$ appear to be inconsistent. The interplay between the localization of the carriers and the strength of the antiferromagnetic correlations is essential. The scattering lifetime obtained from the resistivity measurements and the observed negative magnetoresistance confirm the role of the spin degrees in the scattering mechanism. The correlation between T_c suppression and the parameters characterizing the conduction mechanism suggests that the excitation which interacts with the carriers in the normal state might play an important role in superconductivity. A viable microscopic model for the normal-state properties in the layered cuprates is still lacking. Our interpretations offer a natural explanation for the behavior of the resistivity in a carefully chosen hole-doped *series* of compounds and provide an improved basis for the construction of a proper theory.

ACKNOWLEDGMENTS

J. E. Musa and S. García thank the Conselho Nacional de Pesquisas of Brazil and the Latin American Centre of Physics for financial support.

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